Pittsburgh, Pa.,
Carnegie Inst.of Tech.
30, May 1932.

FROM: Lieut.(jg) H. O. Dahlke, U. S. N.
Lieut.(jg) W. S. Newton, U. S. N.

TO: Head of Post Graduate School.

SUBJECT: Thesis.

1. Enclosed herewith is copy of Thesis presented as required for degree of Master of Science in Metallurgical Engineering, at Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

H. O. DAHLKE,
W. S. NEWTON,

INTRODUCTION.

This thesis presents the results of dilatometric observations made on a series of corrosion resistant chromium steels, some of Navy specification composition, and some of standard commercial analysis. Chromium ranges from 13 - 17%, carbon from .10 to .90%; with and without various amounts of added elements, such as copper, nickel, manganese and molybdenum. The corresponding microstructure, hardness and charpy impact values are described in the thesis presented by Lieutenant G. A. Holderness, U.S.N., and Lieutenant (jg) W. C. France, U.S.N.

The observation and study of phase change by means of the dilatometer has many advantages. Of primary importance are the following: With the same set up changes in volume are easily and rapidly observable over temperatures ranging from 900° C to liquid nitrogen. Small variations in the established rate of heating or cooling do not introduce errors. It is possible to arrest the observations at any temperature and observe the effect of time upon the

transformation. Of major importance also is the ease with which dilatometric curves can be used as a check and to correlate the observations made by X-Rays on the phases present at any temperature. Space lattice dimensions can be corrected to any temperature (if determined at any other temperature by X-Ray data) by the expansion observed. By following calculations of this type an interesting point on the allotropy of iron is observed.

To illustrate this, consider the change from alpha (α) which is body centered cubic to gamma (γ) which is face centered cubic. The atomic volume for the alpha phase $d^3/2$, where "d" is the parameter of the unit cell, and for the gamma phase is $d^3/4$, since there are respectively two and four atoms in the unit cell. If this volume is to remain constant $d^3(\alpha)/2 = d^3(\gamma)/4$ or $d(\gamma) = \sqrt[3]{2} \times d(\alpha)$. $d(\alpha)$ corrected for thermal expansion by means of dilatometric data is 2.894 $\mathring{A}$ at 900° C (1650° F) ($\mathring{A}$ = Angstrom Unit = 10^{-8} cm.). Then $d(\gamma) = 1.26 \times 2.894 = 3.646$ $\mathring{A}$ the lattice dimension for gamma iron. Consider that the least interatomic distance remains

unchanged then d (γ) = $\sqrt{3/2}$ d (α). d (γ) - $\sqrt{3/2}$ x 2.894 = 3.545 Å. On this basis the contraction should be 0.101 Å or 2.8% since the observed contraction is only 0.3% the actual lattice dimension for the gamma phase is 3.646 x (1 - 0.003) = 3.635 Å. From this, the lea t interatomic distance for the gamma phase is 3.635 x $\sqrt{2}/2$ = 2.57 Å and for the alpha phase is 2.894 x $\sqrt{3}/2$ = 2.51 Å. Then the change from alpha to gamma is accompanied by an increase in the least interatomic distance of 0.06 Å in spite of the observed decrease in volume.

Dilatometric studies also permit estimation of volume changes, calculation of amount of phases present at any temperature, behavior of materials below room temperature, comparison of coefficients of expansion and contraction by slopes of heating and cooling curves.

APPARATUS.

The dilatometer used is a modification of one endorsed by the Bureau of Standards. The specimen

Apparatus Continued -

used was a solid cylinder about one-half inch in diameter with an effective length of one inch, having a slot cut in the top into which the thermo couple bead was secured. The thermocouple was nickel - Constantan carefully calibrated used in conjunction with standard Leeds and Northrup potentiometer and galvanometer. The dilatometer consists of a quartz tube, 18 inches long, sealed at the lower end by a flat quartz plate. On this plate rests a one inch length of quartz tubing, on which rests the specimen. On top of the specimen is another quartz tube which transmits the dilatation of the specimen to a dial gauge. Both ends of the specimen were cut to smaller diameter to insure seating and centering in the quartz tube. The gauge is connected to the outside quartz tube by the device described by the Bureau of Standards. This assembly is cemented in a hole in a brass plate upon which a belljar is placed. The thermocouple wires were run through a two hole refractory tubing, led through the brass plate and sealed with a vacuum gutta-percha cement which also served as electric insulation. The brass plate also has a hole for connection to a vacuum pump. The gauge made ten revolutions for a total measure of 0.1 inch.

Apparatus Continued -

A small resistor type furnace was used. Arranged so that it could be moved up or down over the outside quartz tube. The furnace windings was such as to render it very sensitive to changes in power.

In making observations the current was applied at such a rate as to give an increase of 0.1 millivolt per 1.5 minutes. It was cooled at the same rate.

It will be seen from the above that this apparatus meets the more desirable requirements. The apparatus should be useable from about 900° C to well below room temperature. The lower temperatures being easily attained by substituting a Dewar Flask of liquid nitrogen for the furnace. The device for indicating volume change permits quick and easy reading and is capable of following rapid changes. The vacuum system protects the sample from oxidation and eliminates errors due to this cause. The manner of heat application and small length of specimen insure its being at a uniform temperature throughout.

Apparatus Continued -

This method of observing dilatation, while not the most accurate, does permit rapid and direct reading of changes in length over a fairly large range with a high degree of sensitivity.

DESCRIPTION OF SAMPLES.

Samples are wrought alloy steels, of stainless type, and find very diversified application. For moderate resistance to nitric acid, for exposure to atmosphere, fresh water and sea water, when a thin corrosion film that does not penetrate is not objectionable, for the food products and other chemical industries, steam turbine blading, they are functioning satisfactorily. Stainless steel has been the standard for immunity to the attack of fruit and vegetable juices, and other organic substances, in the manufacture of cutlery, dental and surgical instruments, etc., but are being displaced by higher carbon, higher chromium alloys.

Chromium steels are subject to a number of inherent defects that must be guarded against in fabrication and in use if their good qualities are to be preserved. Because of air hardening properties, iron

chromium alloys containing less than 14 Cr cannot be welded unless subsequent annealing is permissible. Likewise in hot riveting the rivets should not be heated above about 1500 degrees F for driving. This air hardening also creates manufacturing difficulties to a slight degree in stainless iron, but to even a greater degree in stainless steel. With Cr about 14% and C low, high temperatures for hot working (over about 2000° F) produce grain growth and brittleness that can be corrected only by severe reworking at correct temperature. With steel containing over 15 Cr, welding produces grain growth and brittleness that cannot be corrected by annealing. For riveting, temperatures should be below 1500° F, especially if the silicon is high, otherwise similar conditions result. Also in low carbon, high chromium (16% or over), long duration of heating between 840 and 1020° F produces on subsequent cooling a high degree of brittleness rendering this steel unfit for operating temperatures within this range. These steels are rather sensitive to drawing temperatures. Tempering at about 1000° F from the as quenched or as

rolled condition produces marked susceptibility to corrosion and weakness in impact. This is accompanied by a lower hardness, a weakening in proportional limit and general break down of the metal.

The Navy uses material of this type for structural work, principally on submarines. Although corrosion-resisting steel is just as well suited for similar work on other classes of vessels, its high cost has not warranted as extensive use on the larger ships.

Some of the applications for which corrosion-resisting steel has been used or for which it is considered suitable for use are listed as follows:

Periscope tubes.

Bolts, studs, nuts, shafts, pins, valve stems, piston rods, and operating rods for inaccessible gear.

Studs, washers, and nuts on manhole covers in inner bottoms.

Hinge pins for water-tight doors, rollers and gears on sliding doors in bunkers, fire-rooms, and engine rooms.

Rigging screws and turnbuckles, davit fittings, boat stowage parts, and deck fittings.

Latches, ratchets, and pins for capstans.

Propeller shafts, rudder stocks, and pintles for small boats.

Description of Samples Continued -

Working parts on dredges (shafts, rollers, pins, etc.).

Submarine radio and signal masts (5-inch extra heavy pipe).

Cold-rolled hatch springs.

Non-magnetic parts in vicinity of the magnetic compass.

Steel shafts on steering transmissions.

Steel parts on telemotor and gyro pilot mechanisms.

Steel parts on emergency steering system.

Clearing lines, submerged anchor cables, and towing bridles on submarines.

METHOD OF OBTAINING AND RECORDING DATA.

Each sample was mounted in the dilatometer, care being taken to insure proper seating and no lost motion due to slip of gauge, etc. Electrical energy was supplied to the furnace at such a rate as to produce an increase of one millivolt (about 15°C) temperature per 1.5 minutes. Cooling was at the same rate. Time, temperature, and percent elongation readings were taken to insure this. The potentiometer was standardized at frequent intervals during the run. Each sample was run twice without removing from the dilatometer. The second curve was checked against the first and used as representing the true conditions.

CURVES A - X - E.

Sample X differs from A by 0.9 more Cr. The effect of this is shown by displacing alpha - gamma transformation from 812° C to 819° C and displacing end point of gamma - alpha from 703° C to 753° C. These temperature comparisons and relative size of hysteresis loops show that the effect of added Cr is to lessen the amount of gamma phase and raise the temperatures of the transformations as shown by Krivobok and Grossman in their work on Fe, -Cr, -C system. Sample X shows almost a reversible transformation, hence the narrow hysteresis loop.

Sample A has .24 less carbon than E, being otherwise the same. With that Cr and C content of E we have practically the eutectoid composition of Fe - Cr - C system. With the increased C content we have more gamma phase present than A, consequently the alpha - gamma transformation is more marked, taking place at 786° C (figure 3) curve 1, compared to 826° C (figure 2) curve 1. The lower transformation takes place at 374° C compared to 734° C. It is interesting

to note two distinct transformations in the cooling curve. In each one of the transformations the sample stopped contracting and actually expanded, although the intensity of each transformation was different and was not as great as it might have been if the transformation had completely taken place at one temperature. Investigation of the split transformation on cooling was made as follows: Run 2 (figure 3, curve 2) was made by heating specimen through alpha - gamma transformation, no curve being plotted for the heating, but using uniform heating rate as before, and on cooling was held for one-half hour at 700° C, near the upper transformation point. On further cooling the gamma - alpha transformation did not occur. Run 3 (figure 3, curve 3) was then made and after alpha - gamma transformation had taken place on heating, specimen was held at 935° C for one-half hour and cooled normally again showing split transformation, however, suppressing slightly the upper transformation and increasing the intensity of the lower. The first break on cooling coming at 709° C

instead of 728° C, the second break on cooling coming at 368° C instead of 380° C. The slope of run 2 (figure 3, curve 2) after the transformation on cooling is similar to run 3 after the latter's lower transformation on cooling at 368° C, showing that the gamma - alpha transformation of run 2 took place at one temperature when sufficient time had been allowed. An additional run was made on E at this time, the sample was heated as before to 935° C, no heating curve being plotted, and on cooling was held for two hours at the same temperature (700° C) where it was formerly held one-half hour. Since the curve is essentially the same, it was not plotted. The complete gamma - alpha transformation took place as before, this time followed by a contraction of .005%, presumably showing the precipitation of carbides at this temperature. It is unfortunate that the apparatus failed at this point, making it impossible to obtain a cooling curve for comparison with that previously obtained. The writers believe that the difference in slope, between run 2 cooling curve and run 1 heating curve, to be due to

carbide precipitation.

Four impact specimens were made of steel E and treated as follows: All four were heated to 940° C and furnace cooled. Two specimens were quenched from above the upper transformation point on cooling at 800° C, and two just below the starting point for the transformation at 703° C.

The results were as follows:

Quenched from 800° C (figure 13)	Quenched from 703° C (figure 12.)
Impact 4.1 ft. lbs.	Impact 37.2 ft. lbs.
Hardness 45.5 Rockwell C.	Hardness 9 Rockwell C.

Showing that at 800° C the structure, on quenching, is by nature Martensitic which accounts for the alloys being hard and brittle. At 703° C the structure is essentially Troostitic or Sorbitic with the carbides precipitated. The accompaning photomicrographs help to confirm this. The results of the impact values show that heat treating range is narrow between 700° C and 800° C, and the time necessary to bring about these changes is quite small, being about one-half hour.

The split transformation is explained as due to increased carbon content stabilizing the gamma phase

and the effect of the cooling rate. It is obvious from our findings that with an infinitely slow cooling rate the complete transformation should take place at about 720° C. With a drastic quench the transformation will be suppressed until about 370° C is reached. With the intermediate rate used , the transformation starts at the higher temperature but is prevented from continuing by further cooling of the sample, producing a metastable super-cooled state, whose tendency to transform becomes more and more intense as the temperature falls, until it overcomes all opposition and transformation again starts and is completed at the lower temperature.

The contraction on precipitation of carbides is explained as follows: The carbon atom is quite large in comparison to the iron atom and its diffusion in solution into the iron space lattice produces considerable distortion. The carbide molecules do not exist as such in the solid solution, but as carbon atoms associated in a definite manner, and definite proportions, with iron and chromium atoms. On coming

out of solution the carbon takes with it the Fe and Cr to form the carbide molecule, which associates itself with other carbide molecules to form sizeable particles. This tends to produce expansion of the sample, but since the iron space lattice is no longer distorted by the presence of carbon and chromium atoms, it contracts to its normal size. This contraction overcomes the expansion caused by formation of carbide molecules and results in a contraction of the sample.

Sample A was cooled to -164° C to determine the effect of low temperature treatment on the transformation temperatures. No change in the transformation temperatures was noted. The change in slope of the heating curve at about 722° C, showing an abnormal expansion, is due to the carbides going into solution. This is true of all curves showing a change of slope at about that temperature. Due to low carbon content this sample does not show the split transformation, although the irregularity of the transformation curve on cooling may be taken as an indication of its presence with higher carbon content as in E.

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CURVES V - A.

(Analysis of figure 5: - Sample V should read - Chromium 12.90% instead of 14%, the rest of the analysis being the same.)

Samples V (figure 5) and A differ only in that sample V has 1.01% nickel content and A has none. The effect of the nickel is to greatly increase the size of the hysteresis loop, shifting the alpha - gamma transformation on heating from 812° C to 740° C and gamma - alpha on cooling from 703° C to 310° C. Showing that the effect of nickel alone is to lower the temperature slightly of the transformation on heating and to lower the transformation temperature on cooling almost 400° C.

CURVES V - X.

Sample V differs from X in chromium and nickel content, the latter having 1% more chromium and no nickel. The effect of 1% nickel compared with 1% chromium is shown by these two samples. Nickel greatly increases hysteresis loop, shifting the alpha - gamma transformation from 846° C to 740° C and the gamma - alpha from 800° C to 310° C, confirming the fact that in these alloys the effect of

1% nickel is to increase the stability of the gamma phase and to lower the transformation points despite the opposite effect of 1% chromium. The effect of 1% nickel is apparently much greater than 1% chromium.

CURVES V - F.

Samples V (Figure 5) and F (Figure 4) differ essentially in sulphur and chromium content, F having .451% more sulphur and 1.8% more chromium.

Sample F was cooled with liquid nitrogen to minus 164° C as in sample A to determine the effect of low temperature treatment. It is seen from curve 2 (figure 4) that cooling below room temperature had no effect on transformation points on cooling or heating.

The effect of sulphur apparently is not noticeable on the transformation points. Comparison of curves V and F show that the alpha - gamma and gamma - alpha transformations take place higher in F due to higher chromium content. Transformations

take place at lower temperature in V due to greater nickel content.

CURVES B - F.

Samples F (figure 4) and B (figure 6, curve 1) are similar except that B has .05% more carbon and F has .452% more sulphur. Sample B shows much more pronounced split transformation than sample F. If, as was already stated, sulphur plays no part in the change of the nature of the transformation, then it may be concluded that the effect of higher carbon is to produce the split transformation and lower the upper transformation on cooling from 795° C to 710° C, the lower transformations being at about the same temperature. The temperatures arrived at were measured on original large scale charts since they could be read more accurately.

The tendency for split transformation in B at about 750° C was further investigated. Sample was heated to above the alpha - gamma transformation point and on cooling was held at 710° C for one-half hour. As shown by the curve 2 (figure 6) most of the transformation took place at this temperature. It is believed

that if sufficient time had been allowed for equilibrium to be reached the lower transformation would have been eliminated as in Sample E.

CURVES B - C.

Sample C (figure 8) differs from B (figure 6) in having 1.33% more Cr and .19% more Ni. The effect of Cr is shown again to raise the transformation point on heating from 710° C to 786° C and higher nickel again to lower the gamma - alpha transformation from 350° C to 324° C.

From previous curves higher Cr results also in raising the temperature of transformation on cooling. Since in the case of alloys B and C, the transformation on cooling is actually lowered, the effect of the difference in Ni content may be considered. Thus even small amounts of Ni have more influence on transformation (cooling) than large amounts of chromium.

CURVES G - C.

Sample G (figure 7) differs from C in having .73% more carbon, slightly higher Cr, and less Ni. The

Curve D Continued -

composition with any other sample. The curve is almost exactly the same as T, indicating that the effect of molybdenum, nickel or copper is practically the same. The transformations take place at the same temperatures and the cooling curves change slope at the same temperatures.

QUENCHED CURVES.

Sample A (curves shown in A', figure 2) was quenched from above the transformation point on heating retaining some of the gamma phase at room temperature. Sample was then heated normally to determine the effect of quenching on the transformation temperature. An error was made in plotting this curve, the origin should be displaced one division to the left. Quenching has no effect on the transformation temperature.

The change of slope noted at about 525° C was further investigated. This temperature also conforms with a drop in impact values of specimens drawn at that temperature.

Quenched Curves Continued -

Three additional samples, V, B, and C (figure 11), were also quenched and heating curves taken. Changes in slope were also noted at about the same temperature in all samples. The slope of the quenched curves differ from that of the unquenched sample and since the coefficient of expansion of gamma and alpha phases differ, and the change of slope at the points noted is an expansion, this must be due to the phase change from gamma to alpha on drawing.

DISCUSSION.

In this investigation we have attempted to cover the effect on transformation points of small amounts of added elements, low temperature, and such heating treatments as quenching on holding at definite temperatures for varying periods of time. It is apparent that low temperatures attained in this study has no effect on the transformations of these samples. Where there is evidence of a split transformation, holding at the temperature for sufficient time where the split transformation first appears, will cause the complete transformation to take place. The effect of quenching, from above critical range, results in no

change in transformation temperatures on heating and cooling, showing that with heating rate used any retained Austenite was decomposed and had no effect on the transformation temperatures. However, irregularities appear in heating curves of quenched samples, as shown in curves 1 and 2 of A', figure 2, also of curves in figure 11, showing that previous heat treatment does effect the slope of heating curve and might influence heat treatment, as drawing, of these samples.

The conclusions drawn from the above investigations agree in substance with those arrived at by a study of the impact and hardness values of the same samples as investigated by Lieutenants Holderness and France. The amount of displacement of transformation temperatures per unit amount of added element should be determined by additional investigation since only the trend of displacement is pointed out here. It is suggested that X-Ray determinations be made to confirm the results of dilatometric study.

SUMMARY AS TO EFFECT OF ADDED ELEMENTS.

CARBON - lowers transformation points on heating and cooling, tends to produce split transformation and increases size of loop.

CHROMIUM - raises transformation points on heating and cooling, and decreases size of loop.

NICKEL - lowers transformation points on heating and cooling, increases size of loop, and counteracts tendency of carbon in producing split transformation.

COPPER - Behaves the same as nickel, but not as markedly.

SULPHUR - No noticeable effect on transformation temperatures.

MOLYBDENUM - Apparently the same as nickel.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Mr. Rose of the Colonial Steel Company, and to the Bureau of Ordnance, Navy Department, for the generous supply of material. To our friend and instructor, Dr. V. N. Krivobok, Research Associate and Professor of Metallurgy, Carnegie Institute of Technology, for helpful suggestions and criticism.

BIBLIOGRAPHY

Krivobok and Grossman, "Influence of Nickel on the Chromium - Iron - Carbon Constitutional Diagram", transactions of the American Society for Steel Treating, September, 1930.

Krivobok and Gensamer, "Dilatometric Study of Chromium - Iron - Nickel Alloys", A.I.M.E. Technical Publication No. 434.

Krivobok and Grossman, " A Study of the Iron - Chromium - Carbon Constitutional Diagram", September,1929.

Strauss, "Metals and Alloys for Industrial Applications requiring extreme Stability", A.S.S.T, August, 1929.

MONYPENY, "Stainless Iron and Steels".

MERRITT, "Effect of Heat Treatment on Corrosion Resistance of Stainless Iron", February,1932.

U. S. NAVY SPECIFICATIONS, for corrosion resisting steel.

NAVY DEPARTMENT, Bureau of Construction and Repair, Technical Bulletin Number 6 -29, September,1929.

P. Chevenard,"Recherches Experimentales Sur Les Allieges De Fer,De Nickel, Et De Chrome, 1927.

Bibliography Continued -

A. E. Lambert, "Stainless Iron and Steel".

Can.Mach.and Mfr., "News volume 40, No. 17,August 28, 1919.

B. E.Main, "Alloys and Constituents of Stainless Steels", A. S.M. E. Vol. 14.

Jeffries and Archer, "Science of Metals".

Aborn and Main, "Nature of Nickel,Chromium,Rustless Steels", A. S.S.T. Vol. 15.

O. K. Parmiter, "High Chromium Steels",A.S. S.T.Vol. 15.

A. Beyer, "Heat Treatment of Stainless Steel".Maschinen Konstrukteur Volume 62, Number 11,June, 1929.

E. Cartel and K. Barth, "Influence of Molybdenum and Silicon on Properties of Stainless Steel", Stahlund Eisen, Volume 47, Number 18, May 5, 1927.

E. R. Fallin, "Systematic Views of Stainless Steel",Iron Age, Volume 111, Number 11, March 13, 1923.

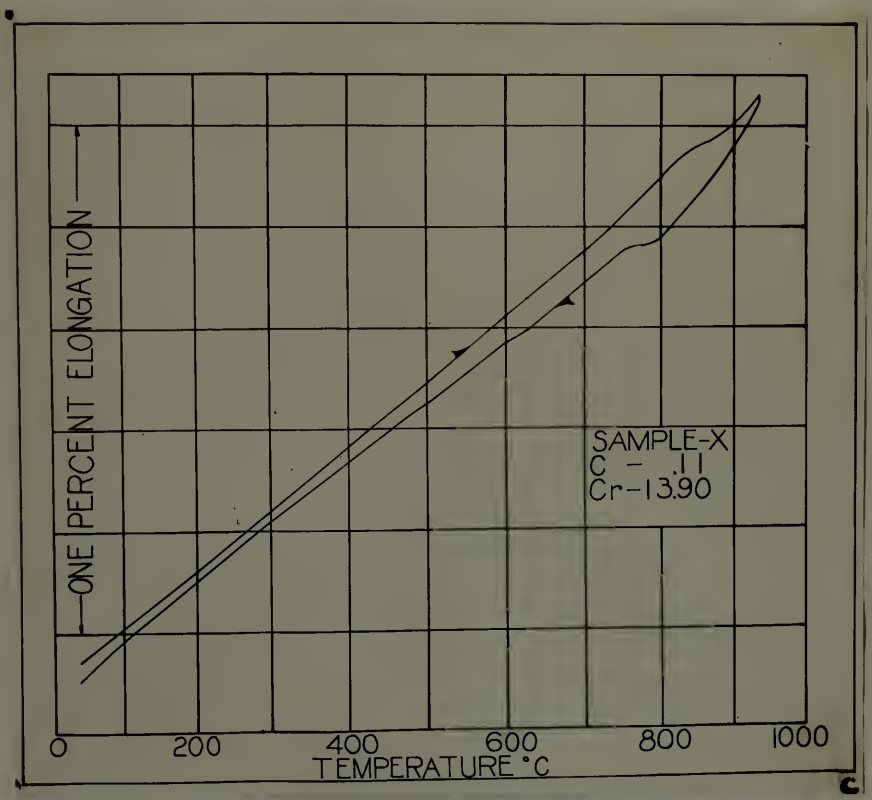

ONE PERCENT ELONGATION
SAMPLE-X
C - .11
Cr-13.90
0
200
400
600
800
1000
TEMPERATURE °C

FIGURE 1.

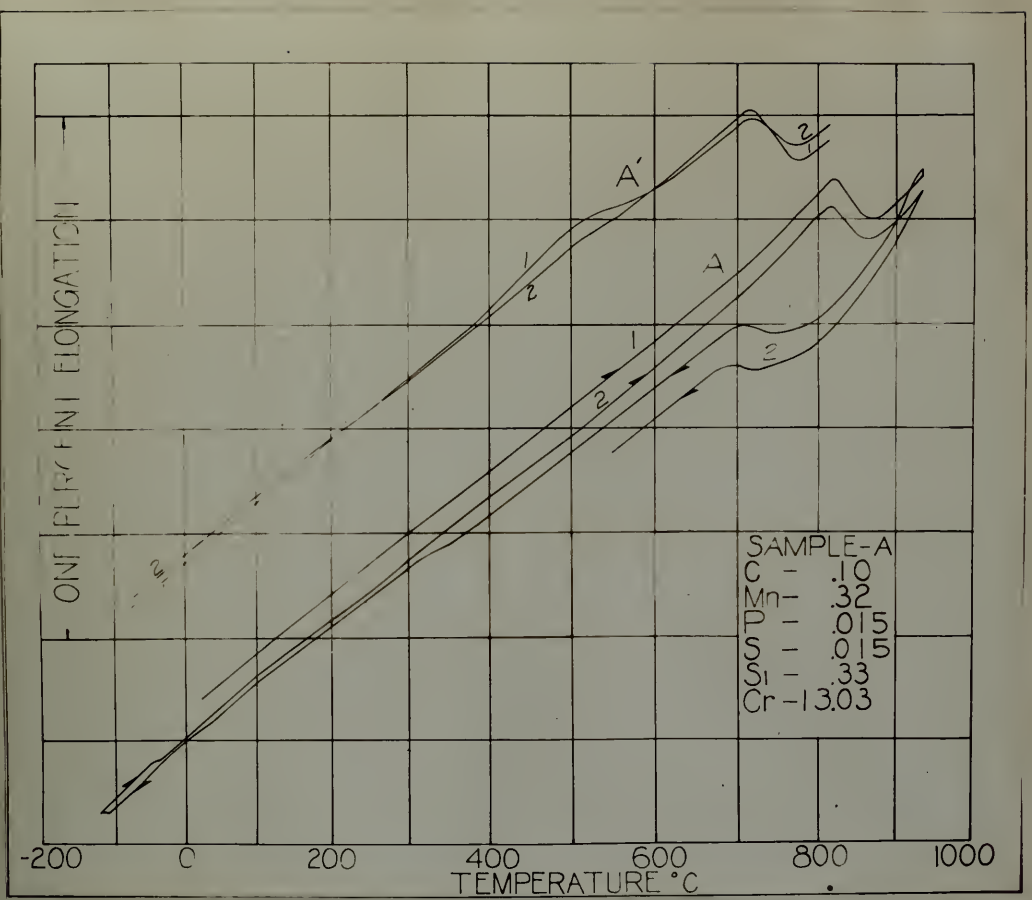
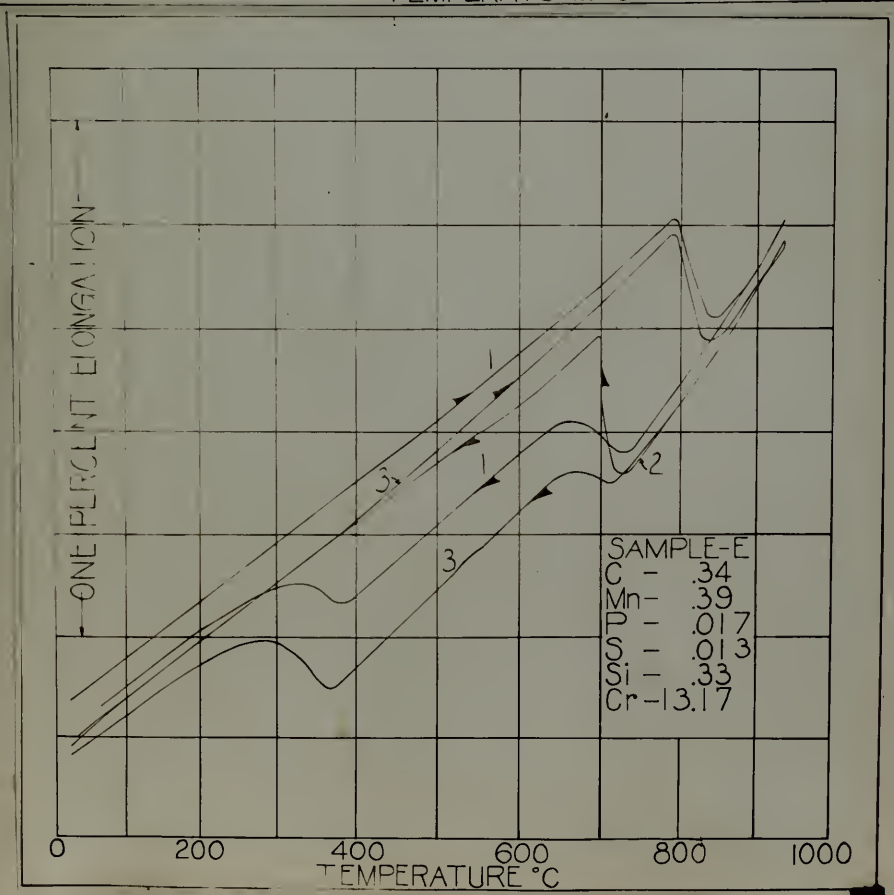


FIGURE 2.



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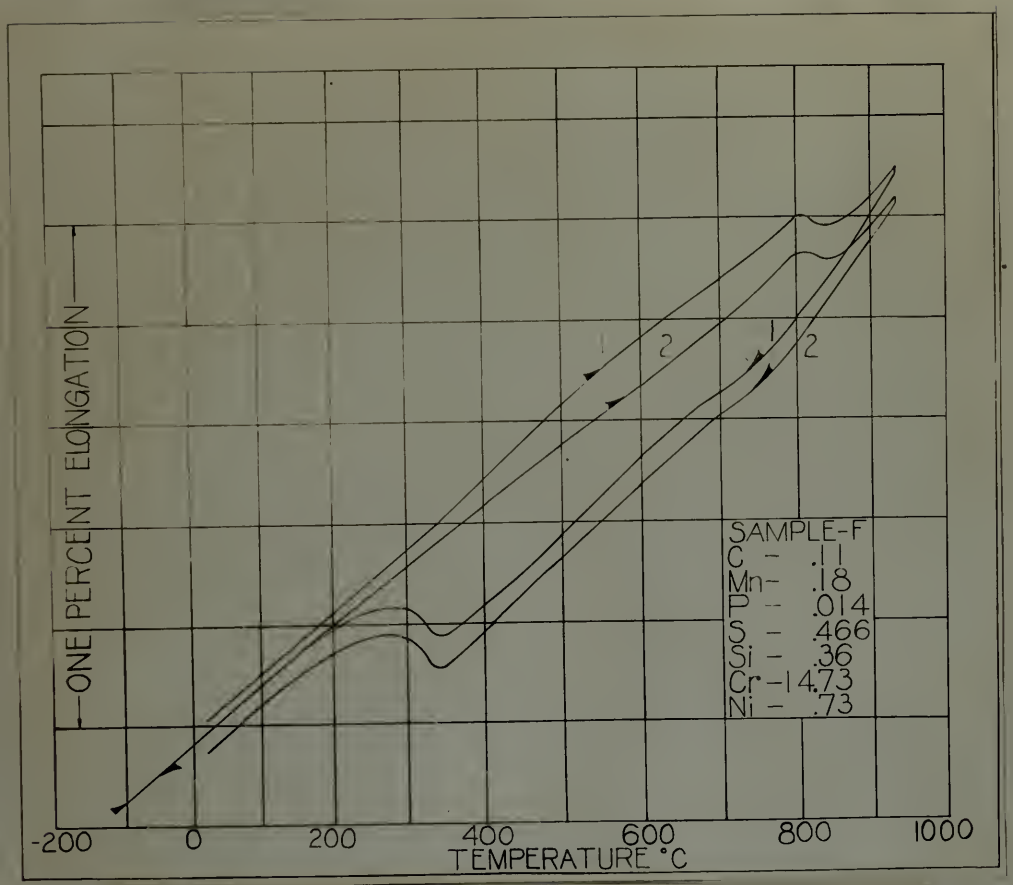

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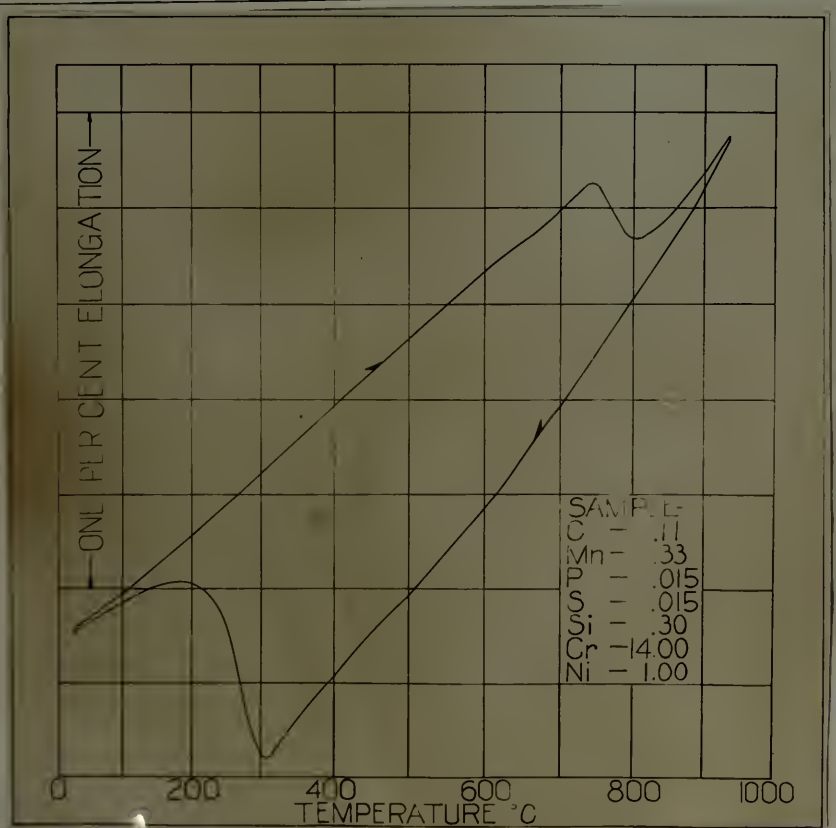


FIGURE 5.

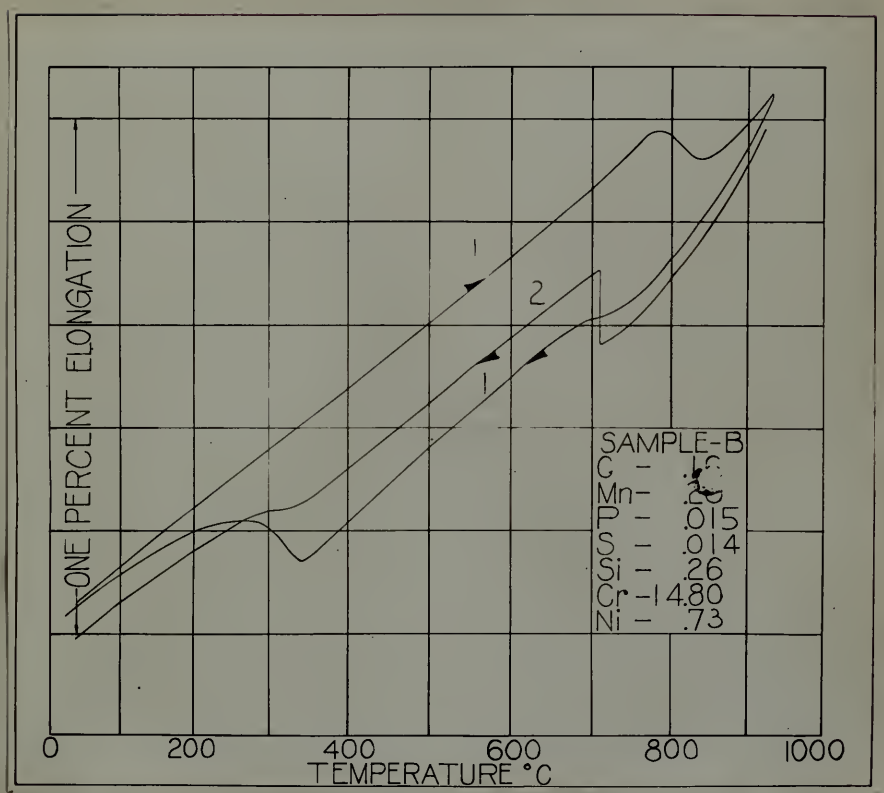

ONE PERCENT ELONGATION
1
2
1
SAMPLE-B
C - .15
Mn - .50
P - .015
S - .014
Si - .26
Cr - 14.80
Ni - .73
0
200
400
600
800
1000
TEMPERATURE °C

FIGURE 6.

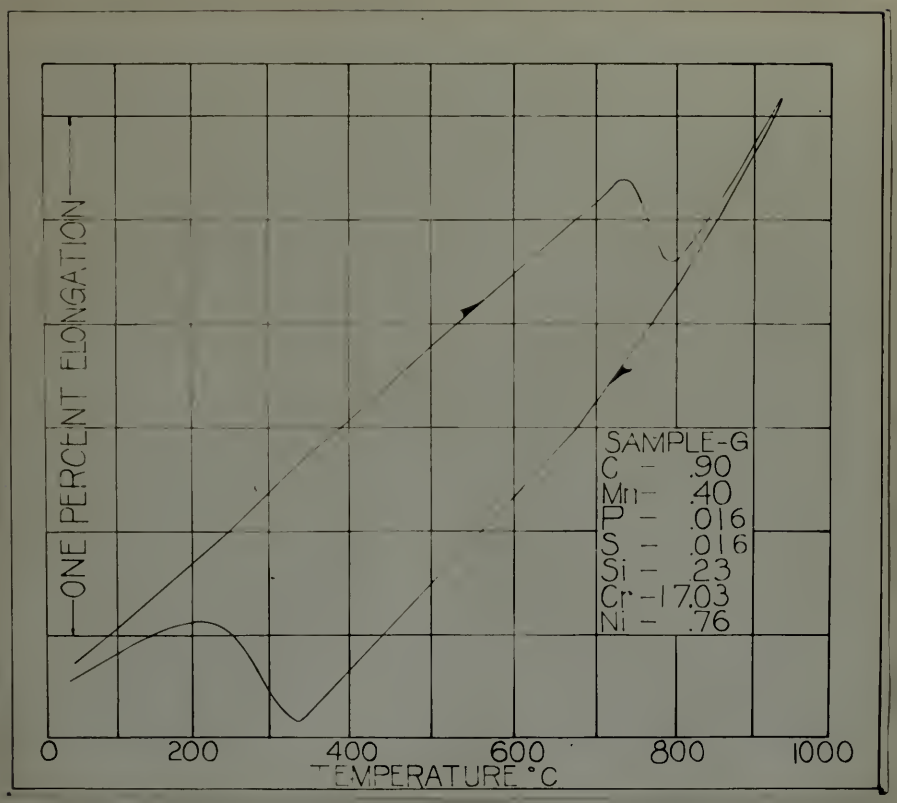
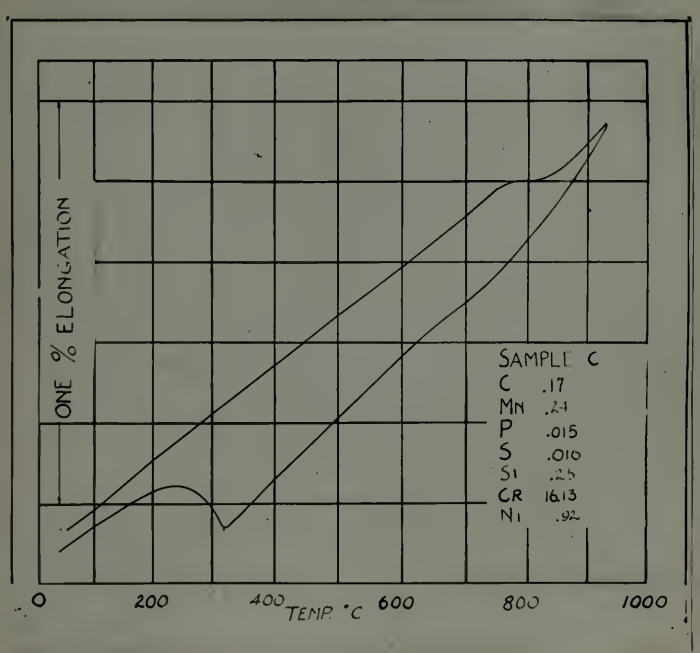


FIGURE 7.



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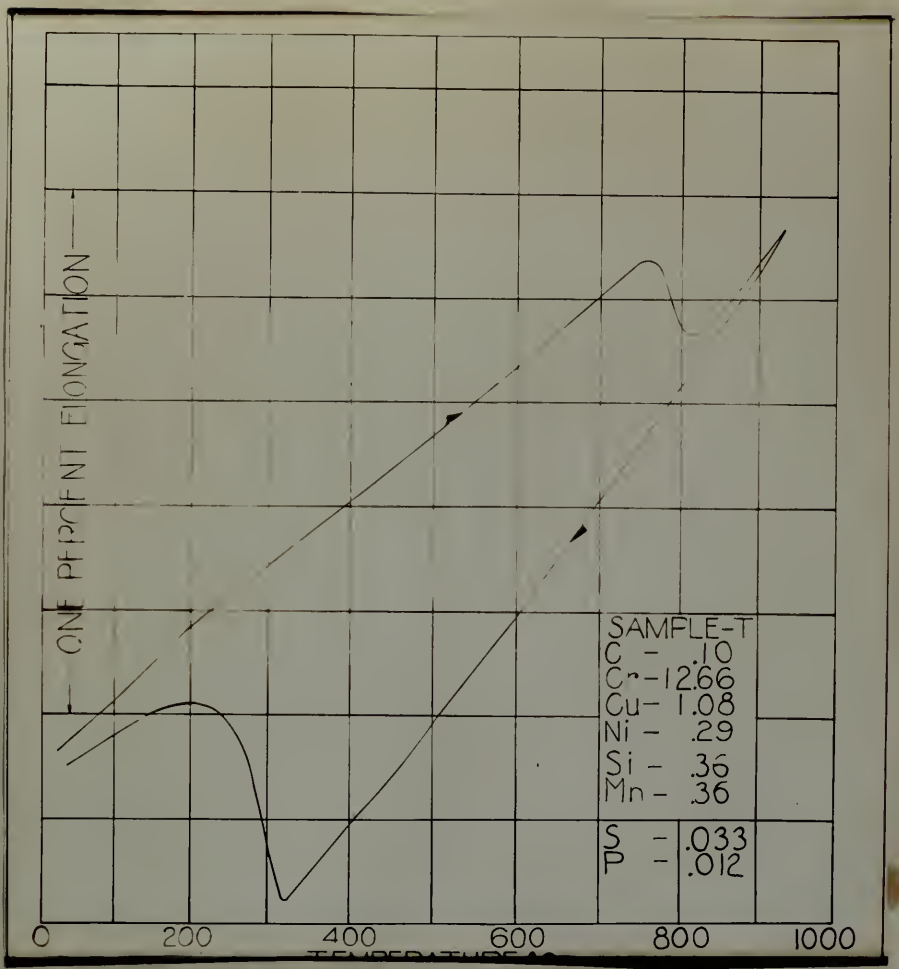

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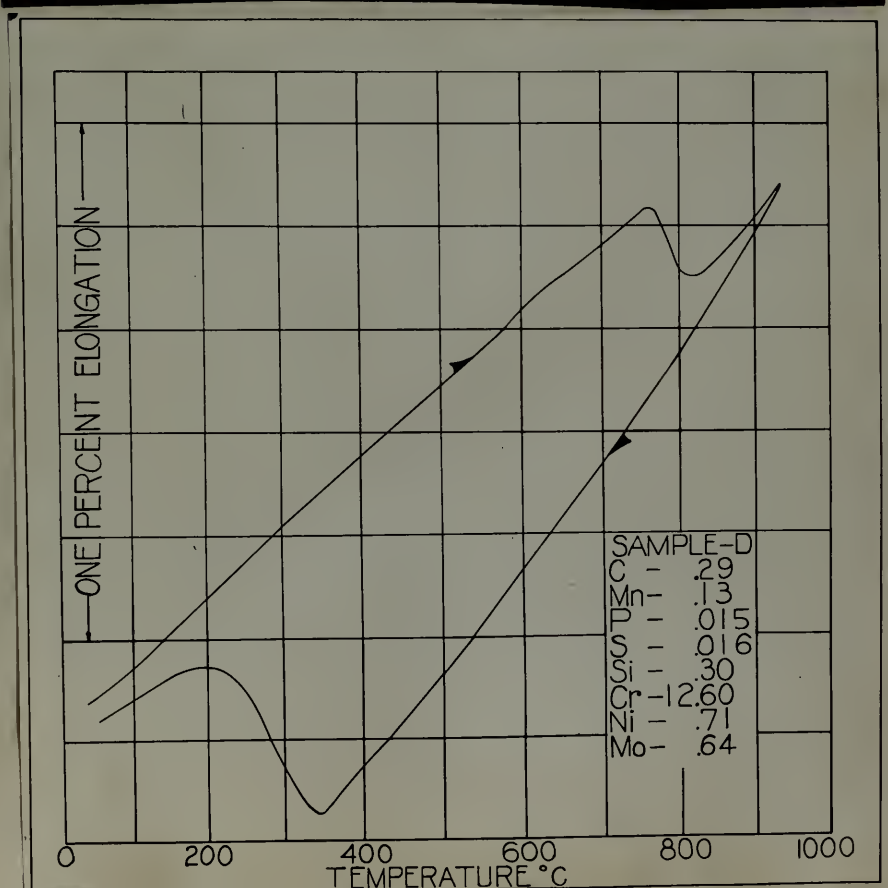


FIGURE 10.

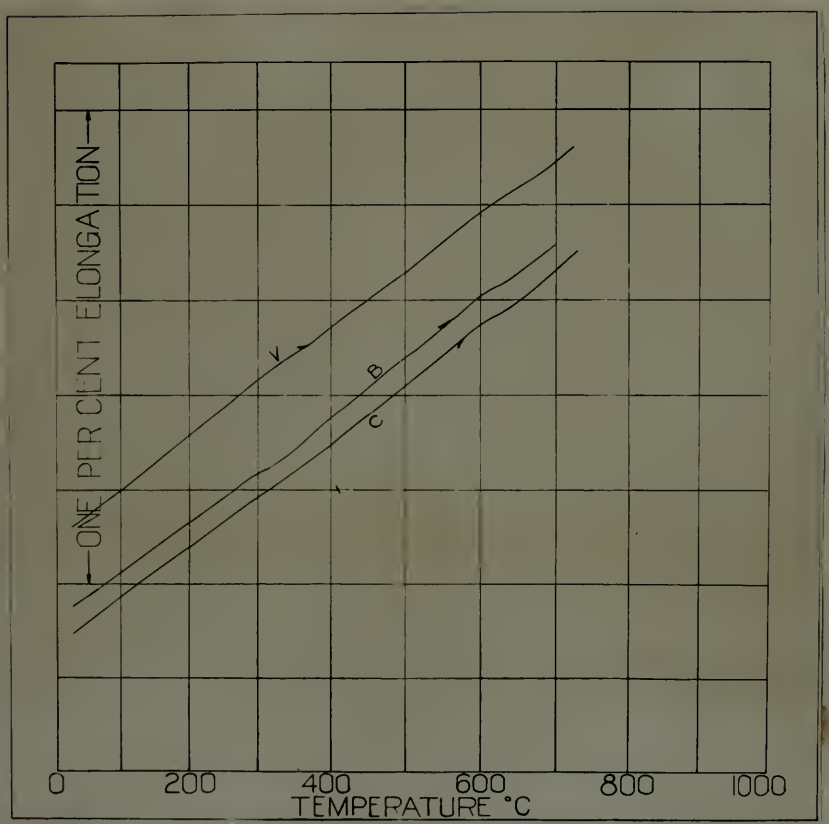

ONE PER CENT ELONGATION
A
B
C
0
200
400
600
800
1000
TEMPERATURE °C

FIGURE 11.

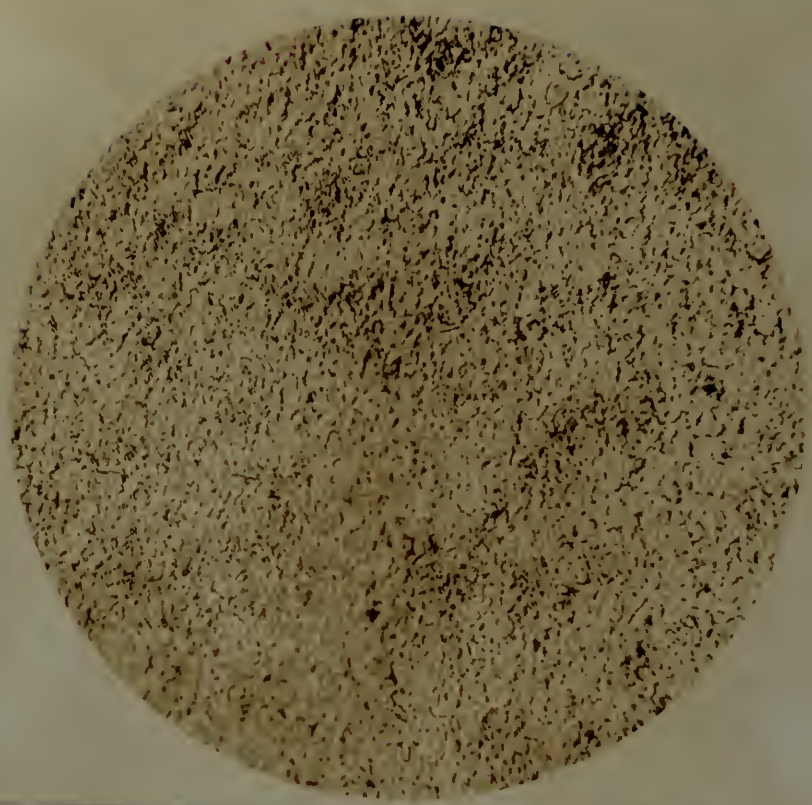


Figure 12,

X 400.

Steel E
Quenched
from 703°C

Etched
Ferric
Chloride.

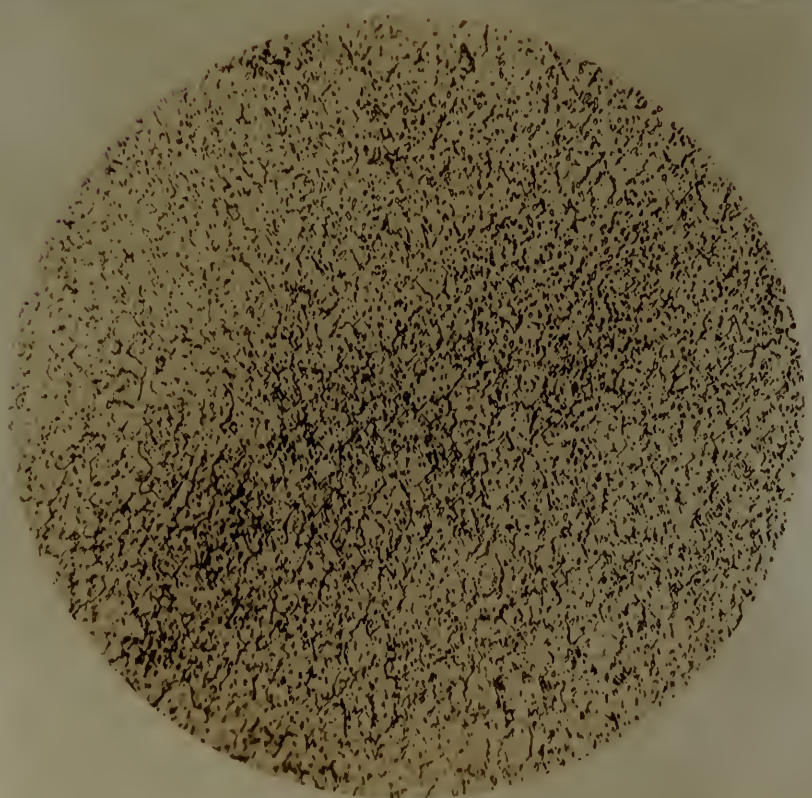


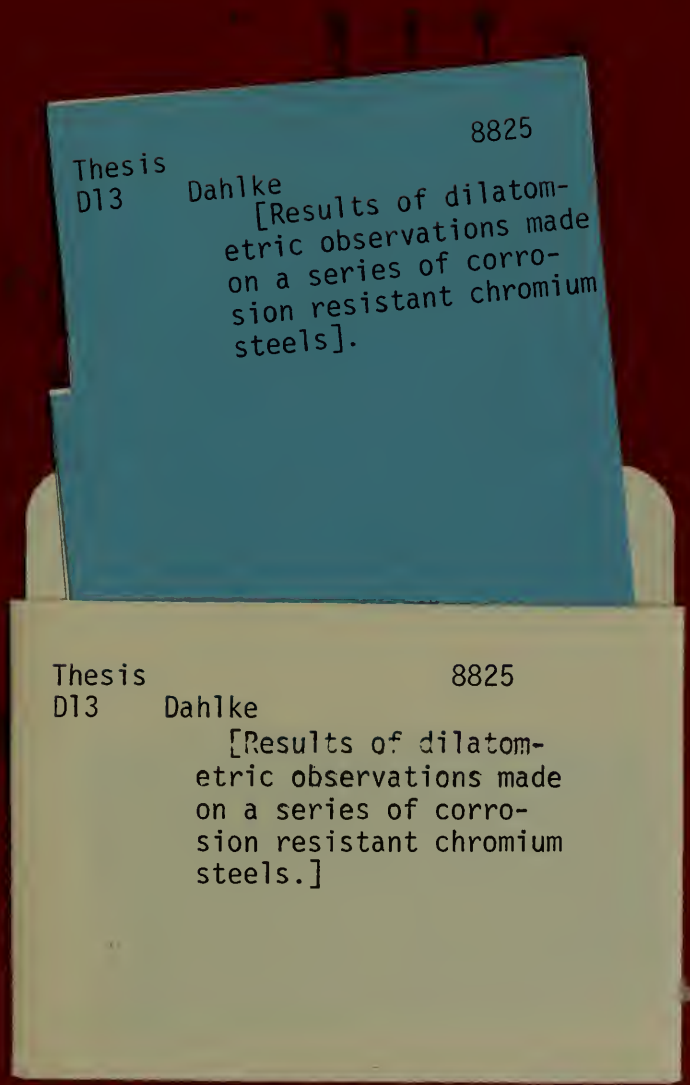
Figure 13,

X 400

Steel E
Quenched
from 800°C

Etched
Ferric
Chloride.

DATE DUE			


8825
Thesis
D13 Dahlke
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